

CANDIDATE
NAME

CENTRE
NUMBER

--	--	--	--	--

CANDIDATE
NUMBER

--	--	--	--

CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

May/June 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **17** printed pages and **3** blank pages.

Answer **all** the questions in the spaces provided.

- 1 (a) Limewater is a saturated solution of $\text{Ca}(\text{OH})_2$ in water. It is used to test for the presence of CO_2 in a gaseous mixture.

(i) Write an equation for the reaction between limewater and CO_2 .

..... [1]

A saturated solution of $\text{Ba}(\text{OH})_2$ can be used instead of $\text{Ca}(\text{OH})_2$ to test for CO_2 . A saturated solution of $\text{Mg}(\text{OH})_2$ cannot be used for this test.

(ii) Explain why a saturated solution of $\text{Ba}(\text{OH})_2$ **can** be used to test for CO_2 .

.....
..... [1]

(iii) Explain why a saturated solution of $\text{Mg}(\text{OH})_2$ **cannot** be used to test for CO_2 .

.....
.....
..... [2]

(b) Describe and explain the trend in the thermal stabilities of the carbonates down Group 2.

.....
.....
.....
.....
..... [3]

(c) Nickel carbonate, NiCO_3 , decomposes on heating.

Use the *Data Booklet* to explain whether NiCO_3 will decompose more or less readily than CaCO_3 .

.....
.....
.....
..... [2]

[Total: 9]

2 (a) (i) Complete the following electronic configurations.

- the cobalt atom, Co $1s^2 2s^2 2p^6$
- the cobalt(II) ion, Co^{2+} $1s^2 2s^2 2p^6$

[1]

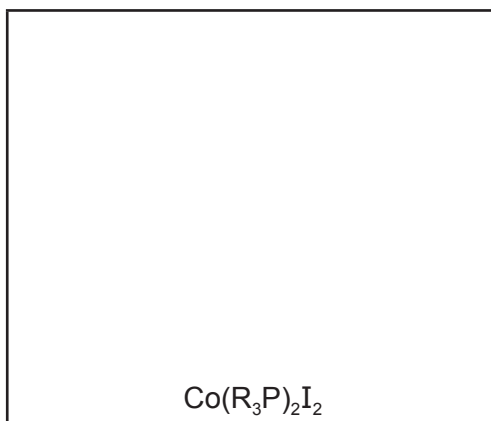
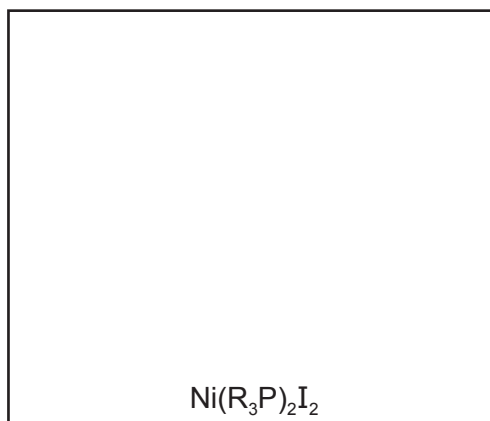
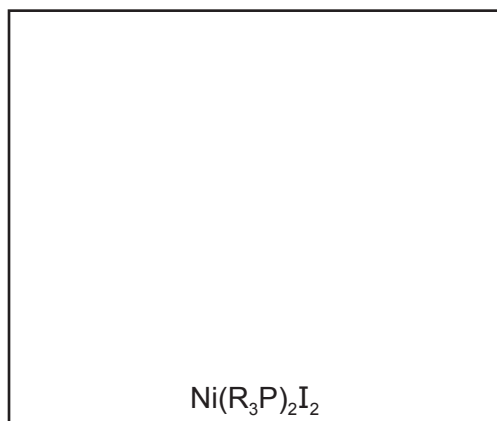
(ii) State the colours you would observe when concentrated $HCl(aq)$ is added to an aqueous solution of cobalt(II) nitrate, $Co(NO_3)_2$.
Give the formulae and geometry of the complexes formed.

.....

 [5]

(b) There are two isomers with the formula $Ni(R_3P)_2I_2$, but only one structure with the formula $Co(R_3P)_2I_2$. (R = alkyl, R_3P is a monodentate ligand)

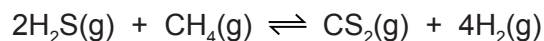
Draw diagrams showing the structure of $Co(R_3P)_2I_2$ and the two isomers of $Ni(R_3P)_2I_2$.



[3]

[Total: 9]

- 3 One method of producing hydrogen from natural gas is the reaction between hydrogen sulfide and methane.



- (a) Write the expression for K_p for this reaction, and state its units.

$$K_p =$$

units
[2]

- (b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.

$\text{H}_2\text{S}(\text{g})$ 200 atm

$\text{CH}_4(\text{g})$ 100 atm

The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $\text{CS}_2(\text{g})$ is 2 atm and that of the remaining $\text{CH}_4(\text{g})$ is 98 atm.

- (i) Calculate the equilibrium partial pressures of $\text{H}_2\text{S}(\text{g})$ and $\text{H}_2(\text{g})$.

$$p(\text{H}_2\text{S}) = \dots\dots\dots \text{ atm}$$

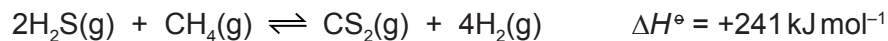
$$p(\text{H}_2) = \dots\dots\dots \text{ atm}$$

[2]

- (ii) Calculate the value of K_p at this temperature.

$$K_p = \dots\dots\dots [1]$$

(c) (i) Predict the sign of ΔS° for this reaction. Explain your answer.



.....
 [1]

The free energy change, ΔG° , for this reaction at 1000 K is $+51 \text{ kJ mol}^{-1}$.

(ii) Calculate the value of ΔS° for this reaction, stating its units.

$\Delta S^\circ = \dots\dots\dots$ units $\dots\dots\dots$ [2]

(d) How would the value of ΔG° , and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

.....

 [2]

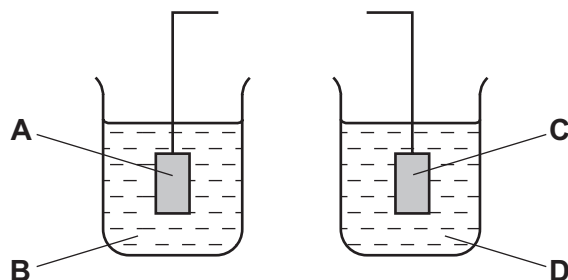
[Total: 10]

- 4 (a) (i) Define the term *standard cell potential*, $E_{\text{cell}}^{\ominus}$.

.....

 [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E_{\text{cell}}^{\ominus}$ for a cell composed of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Ag^{+}/Ag half-cells.



- (ii) Complete the diagram, labelling the components you add. [1]

- (iii) Identify the components A-D.

A
 B
 C
 D [3]

- (b) (i) Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in (a) are connected by a wire and the circuit is completed.

.....
 [1]

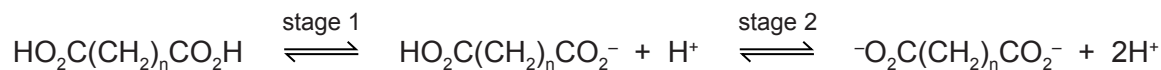
- (ii) Another electrochemical cell was set up using $0.31 \text{ mol dm}^{-3} \text{ Ag}^{+}(\text{aq})$ instead of the standard Ag solution.

Use the Nernst equation, $E = E^{\ominus} + 0.059 \log[\text{Ag}^{+}(\text{aq})]$, and the relevant $E^{\ominus}$ values to calculate the new E_{cell} in this experiment.

$$E_{\text{cell}} = \dots\dots\dots \text{ V [2]}$$

[Total: 8]

5 Dicarboxylic acids dissociate in stages.



(a) The $\text{p}K_{\text{a}}$ values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$	$\text{p}K_{\text{a}}(1)$ for stage 1	$\text{p}K_{\text{a}}(2)$ for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the $\text{p}K_{\text{a}}$ of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, is 4.76.

(i) State the mathematical relationship between $\text{p}K_{\text{a}}$ and the acid dissociation constant K_{a} .
..... [1]

(ii) With reference to the table above, suggest why the $\text{p}K_{\text{a}}(1)$ values

- are all smaller than the $\text{p}K_{\text{a}}$ of ethanoic acid,

.....
.....
.....

- become larger as n increases.

..... [3]

(iii) Suggest why all the $\text{p}K_{\text{a}}(2)$ values in the table above are larger than the $\text{p}K_{\text{a}}$ of ethanoic acid.

.....
..... [1]

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

(i) Explain what is meant by the term *buffer solution*.

.....
..... [2]

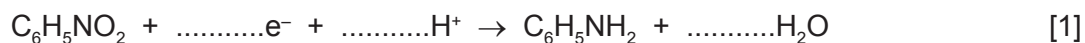
(ii) Write two equations to show how monosodium butanedioate, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na}$, acts as a buffer.

.....
..... [2]

[Total: 9]

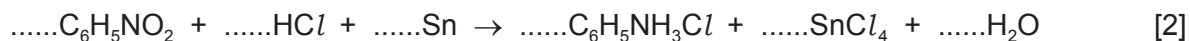
- 6 Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be reduced to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, in acid solution in a two step process.

- (a) (i) Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.



- (ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to (i) useful.



- (b) When 5.0g of nitrobenzene was reduced in this reaction, 4.2g of phenylammonium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = $\dots\dots\dots\%$ [2]

- (c) Following the reaction in (b), an excess of NaOH(aq) was added to liberate phenylamine from phenylammonium chloride.

- (i) Calculate the mass of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, produced when 4.20g of phenylammonium chloride reacts with an excess of NaOH(aq) .

mass of phenylamine = $\dots\dots\dots\text{g}$ [1]

The final volume of the alkaline solution of phenylamine in (i) was 25.0 cm^3 . The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68g of phenylamine.

- (ii) Use the data to calculate the partition coefficient, $K_{\text{partition}}$, of phenylamine between dichloromethane and water.

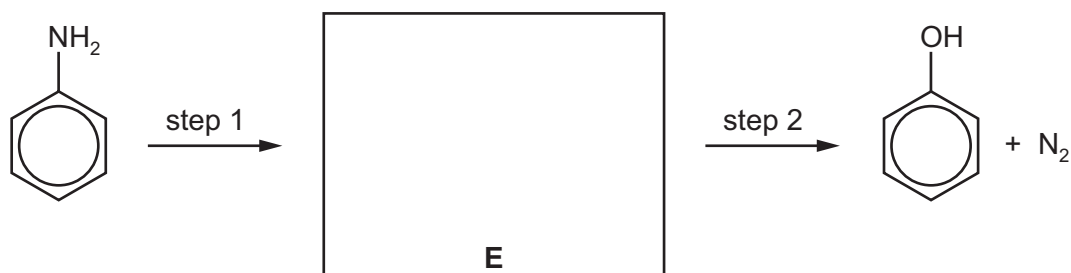
$K_{\text{partition}} = \dots\dots\dots$ [2]

(d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

.....

 [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1

step 2 [2]

(ii) Draw the structure of the intermediate compound **E** in the box above.

[1]

[Total: 13]

- 7 (a) (i) Use the *Data Booklet* to draw the structure of the tripeptide Ala-Ser-Gly showing its peptide bonds in full.

Ala-Ser-Gly

[2]

- (ii) Calculate the relative molecular mass, M_r , of Ala-Ser-Gly.

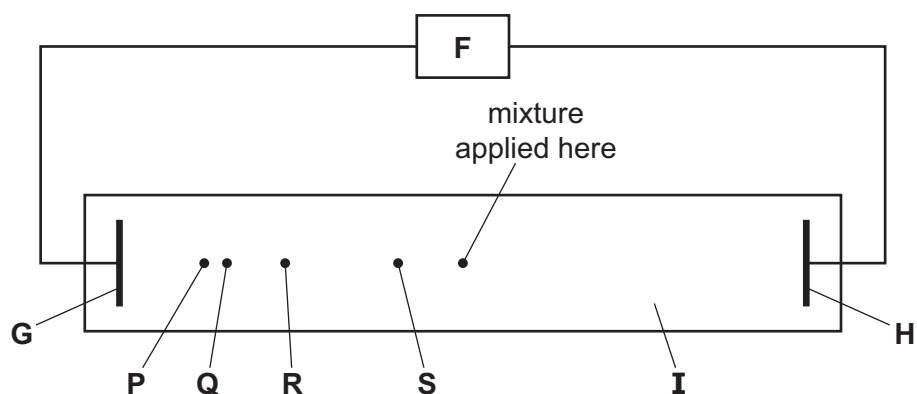
$M_r = \dots\dots\dots$ [1]

- (b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

- (i) Draw the structure of serine at pH 11.

[1]

At the end of the experiment the following results were seen.



(ii) Identify the components labelled **F-I** in the above diagram.

- F**
- G**
- H**
- I** [4]

(iii) Suggest the identities of the species responsible for

spot **P**, ...

spot **S**.

Explain your answers.

..... [3]

(c) (i) State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

..... [1]

(ii) Name the *type of reaction* in (i).

..... [1]

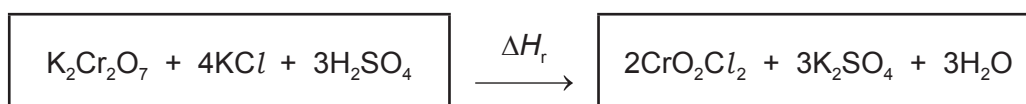
[Total: 13]

- 8 (a) Chromyl chloride, CrO_2Cl_2 , can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.



Use the following data to complete the Hess' Law cycle and calculate the enthalpy change of the reaction, ΔH_r .

compound	enthalpy change of formation, $\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{K}_2\text{Cr}_2\text{O}_7$	-2061
KCl	-437
H_2SO_4	-814
CrO_2Cl_2	-580
K_2SO_4	-1438
H_2O	-286



elements

$\Delta H_r = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

(b) There are two isomeric complex ions with the formula $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$. One is green and the other is violet.

(i) Suggest the *type of isomerism* shown by these complex ions.

..... [1]

(ii) Explain why these two complex ions

- are coloured, ...

.....

.....

.....

- have **different** colours.

.....

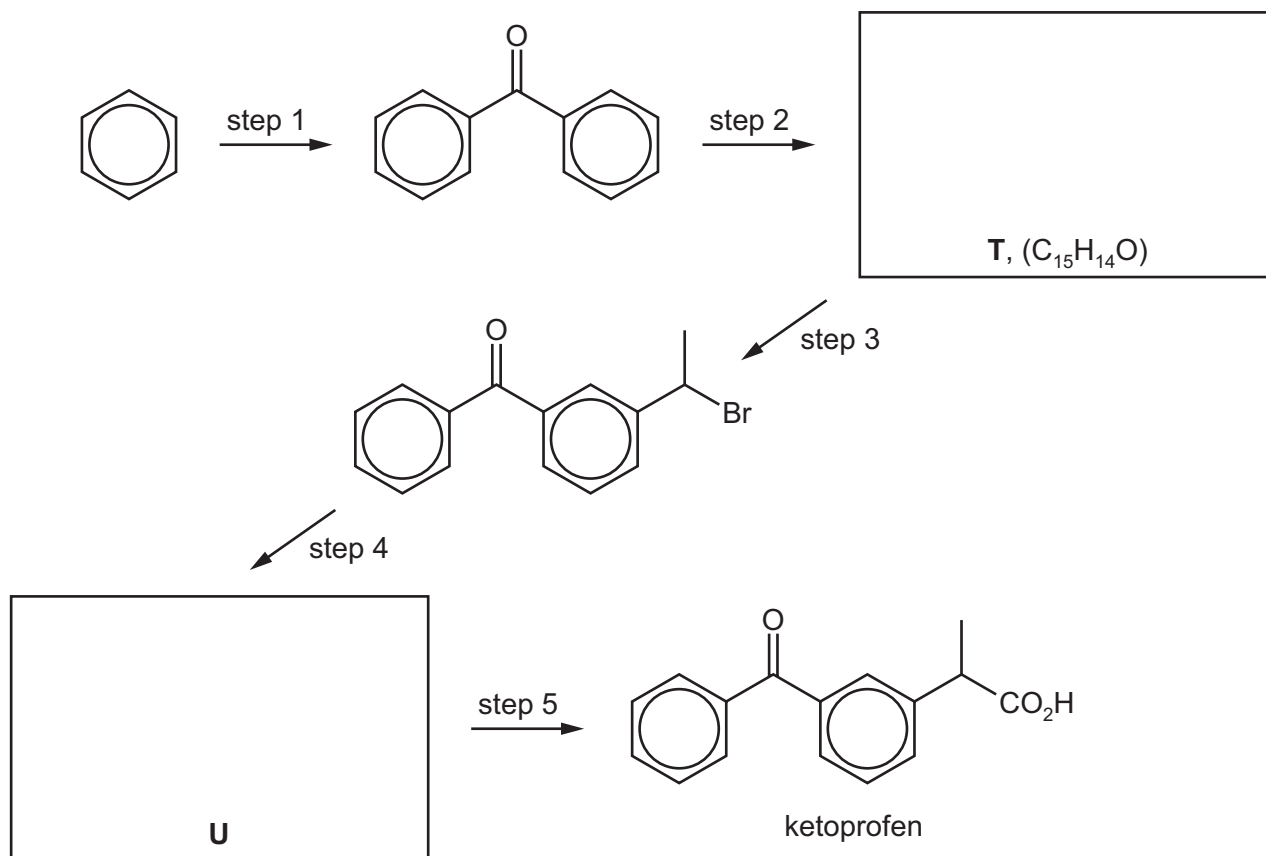
.....

.....

[4]

[Total: 7]

- 9 The anti-inflammatory drug ketoprofen can be synthesised from benzene via the following five steps.



- (a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above.

[2]

- (b) Suggest reagents and conditions for steps 1-5.

step 1

step 2

step 3

step 4

step 5

[5]

- (c) What *types of reaction* are steps 1 and 5?

step 1

step 5

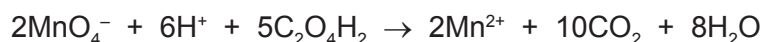
[2]

[Total: 9]

10 (a) Ethanedioic acid, $\text{C}_2\text{O}_4\text{H}_2$, occurs in many vegetables. The amount that occurs in spinach can be estimated as follows.

- 40.0 g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm^3 with water.
- A 25.0 cm^3 portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with $0.0200\text{ mol dm}^{-3}\text{ KMnO}_4$.

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.



In the titration, 15.20 cm^3 of KMnO_4 was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves.

percentage of ethanedioic acid = ... % [3]

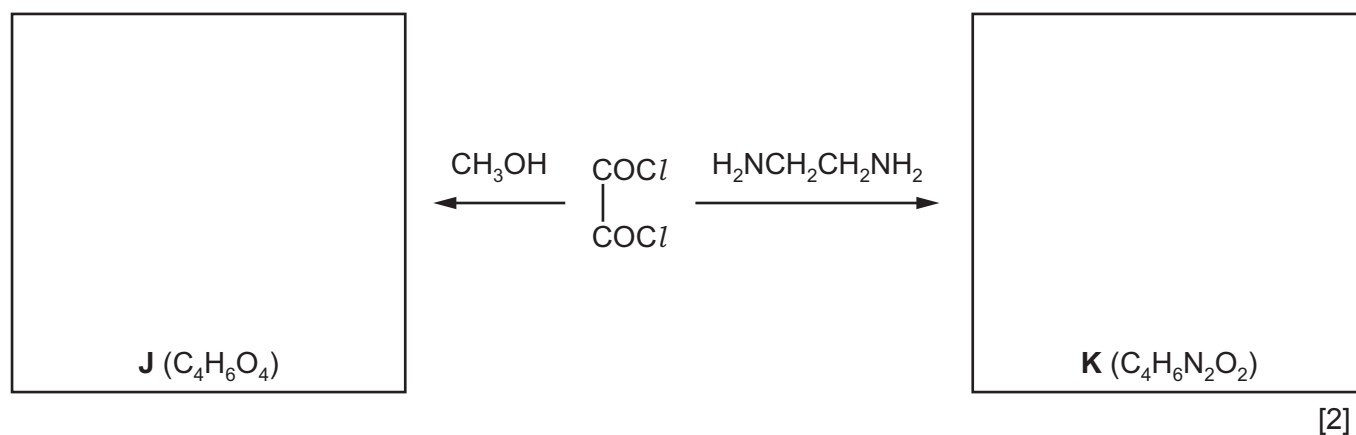
(b) Ethanedioic acid can be converted into ethanedioyl chloride:



(i) State a suitable reagent for this reaction.

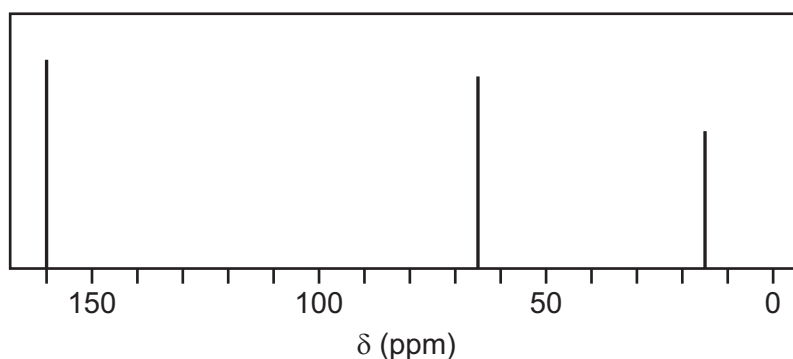
..... [1]

(ii) For the reactions of ethanedioyl chloride below, suggest the structures of compounds **J** and **K** and draw them in the boxes.

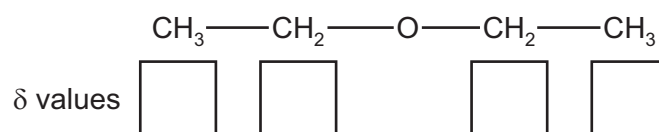


(c) When ethanedioyl chloride is reacted with silver ethanedioate, $\text{AgO}_2\text{CCO}_2\text{Ag}$, in ethoxyethane at -30°C , an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6 .

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, is shown below.



(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.

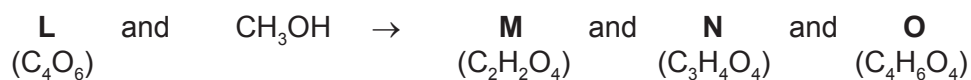


[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.

..... [1]

(d) When pure **L** is reacted with an excess of CH_3OH , a mixture of three compounds is formed.

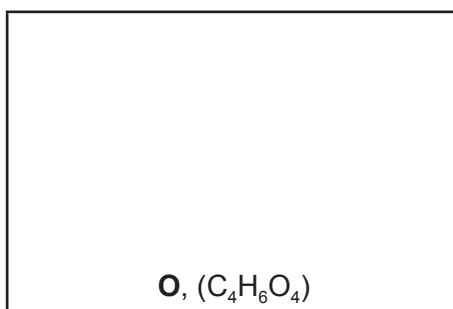
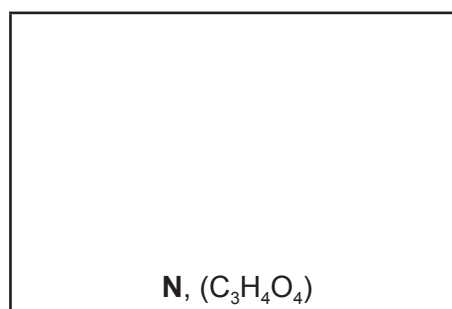
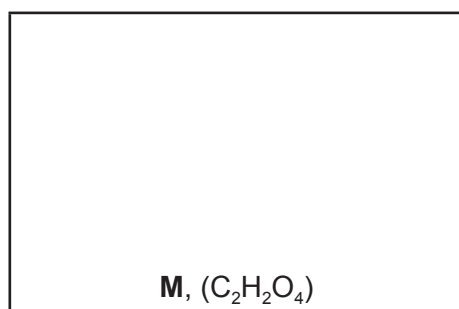


M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

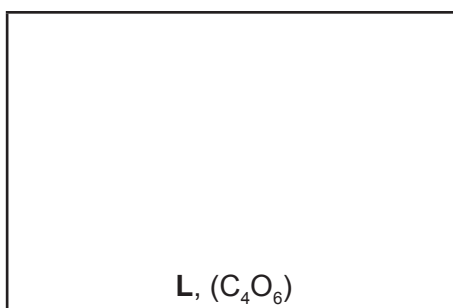
compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Suggest the structures of **M**, **N** and **O**.



[3]

(ii) Suggest a structure for **L** that fits all the data given in (c) and (d).



[1]

[Total: 13]

BLANK PAGE

Permission to reproduce items where third-party owned material protected by copyright is included has been sought and cleared where possible. Every reasonable effort has been made by the publisher (UCLES) to trace copyright holders, but if any items requiring clearance have unwittingly been included, the publisher will be pleased to make amends at the earliest possible opportunity.

To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced online in the Cambridge International Examinations Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download at www.cie.org.uk after the live examination series.

Cambridge International Examinations is part of the Cambridge Assessment Group. Cambridge Assessment is the brand name of University of Cambridge Local Examinations Syndicate (UCLES), which is itself a department of the University of Cambridge.

CANDIDATE
NAME

--

CENTRE
NUMBER

--	--	--	--	--

CANDIDATE
NUMBER

--	--	--	--



CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

May/June 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **20** printed pages.

Answer **all** questions in the spaces provided.

- 1 (a) Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, are formed. In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are **also** bonded to the nitrate ions.

- (i) Suggest the type of bonding that occurs between

H_2O and Mg^{2+} , ...

H_2O and NO_3^-

[2]

- (ii) Describe the arrangement of the water molecules around the Mg^{2+} ion.

..... [1]

- (iii) Describe in detail what you would observe when crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are heated in a boiling tube, gently at first and then more strongly. Write equations for any reactions that occur.

.....

 [4]

- (iv) Calculate the percentage **loss** in mass when $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is heated strongly to constant mass.

percentage loss = ... % [2]

(b) Explain why the Group 2 nitrates become more stable to heat down the group.

.....

.....

.....

.....

..... [2]

(c) Magnesium nitrate and silver nitrate, AgNO_3 , decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition.

Write an equation for the decomposition of AgNO_3 .

..... [1]

[Total: 12]

2 Ethanoic acid is a weak acid.

(a) Explain what is meant by the term *weak acid*.

.....
 [1]

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	$\text{CH}_3\text{CO}_2\text{H}$	4.8
2	$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	4.9
3	$\text{CH}_3\text{CHClCO}_2\text{H}$	2.8
4	$\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a .

..... [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

.....

- acid 2 and acid 3,

.....

- acid 3 and acid 4.

.....

[3]

- (c) (i) Draw a fully labelled diagram of the equipment needed to measure the voltage of an electrochemical cell consisting of the standard hydrogen electrode and the standard Cu/Cu²⁺ electrode.

[4]

- (ii) For the cell drawn in (i), calculate the $E_{\text{cell}}^{\ominus}$ and state which electrode is positive.

$E_{\text{cell}}^{\ominus} = \dots\dots\dots$ identity of the positive electrode $\dots\dots\dots$ [1]

- (d) A monobasic acid, **D**, has $K_{\text{a}} = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$.

- (i) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of **D**.

pH = $\dots\dots\dots$ [2]

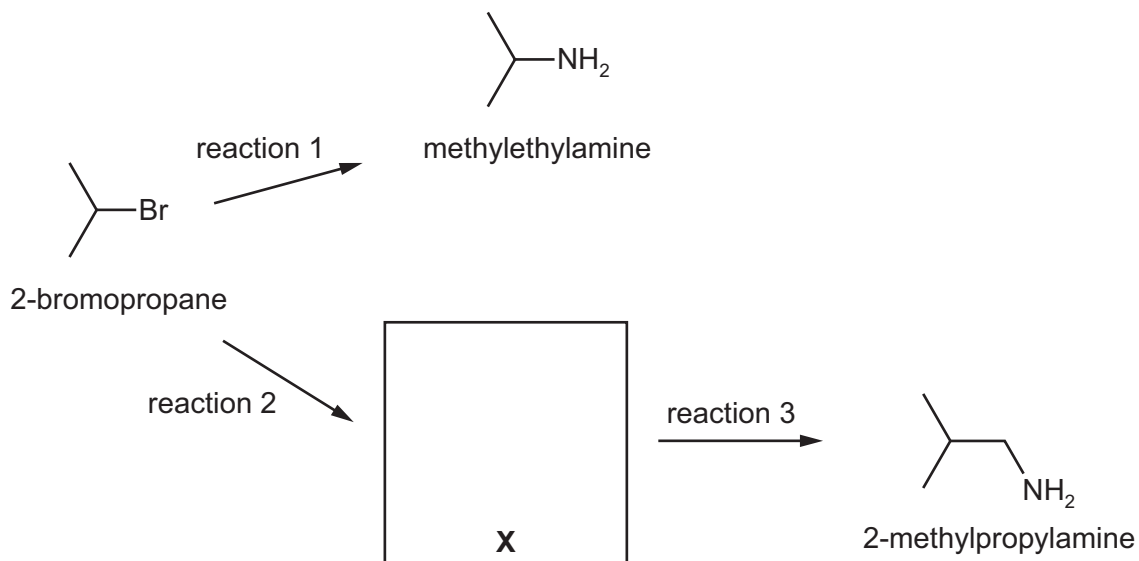
- (ii) An electrochemical cell similar to the one you have drawn in (c)(i) was set up using a $0.100 \text{ mol dm}^{-3}$ solution of **D** in the hydrogen electrode instead of the standard solution.

Use the data and the Nernst equation, $E = E^{\ominus} + 0.059 \log [\text{H}^+(\text{aq})]$, to calculate the new E_{cell} in this experiment.

$E_{\text{cell}} = \dots\dots\dots \text{ V}$ [2]

[Total: 14]

- 3 (a) 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.



(i) Draw the structure of the intermediate **X** in the box above. [1]

(ii) Suggest reagents and conditions for

- reaction 1, ...
- reaction 2, ...
- reaction 3.

[3]

(b) (i) Write an equation showing why aqueous solutions of ethylamine are alkaline.

..... [1]

(ii) Compare the basicities of ethylamine and ammonia. Explain your answer.

.....

.....

.....

..... [2]

(c) Solutions containing mixtures of amines and their salts are buffer solutions.

(i) Explain what is meant by the term *buffer solution*.

.....
..... [1]

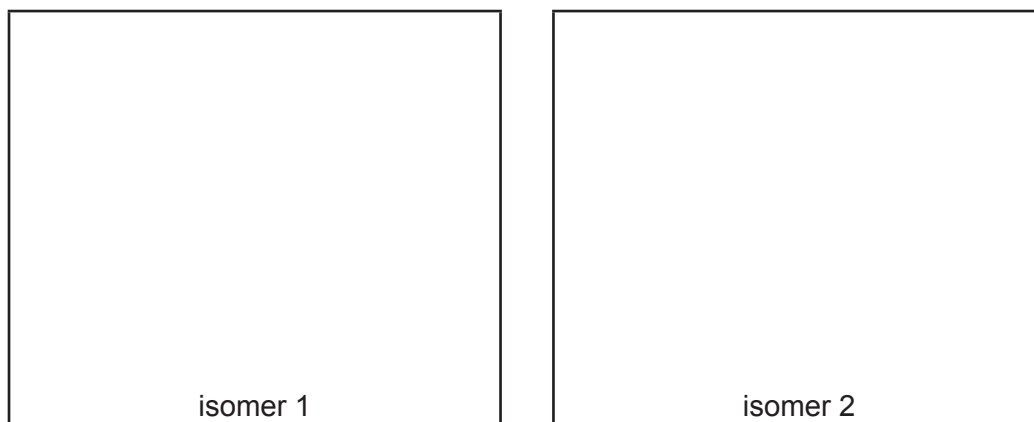
(ii) Write two equations to show how a solution containing a mixture of CH_3NH_2 and $\text{CH}_3\text{NH}_3\text{Cl}$ acts as a buffer.

.....
..... [2]

[Total: 10]

- 4 (a) There are two isomeric complexes with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, one of which is an anti-cancer drug.

(i) Draw diagrams to show the three-dimensional structures of the two isomers.

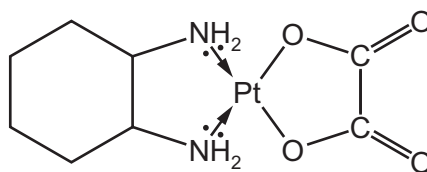


[2]

(ii) Comment on the polarity of the two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Explain your answer.

.....
 [1]

Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.



oxaloplatin

(iii) Explain why there are no isomers of oxaloplatin.

.....
 [1]

(b) Only one structure of the complex $[\text{Ni}(\text{R}_3\text{P})_2\text{Cl}_2]$ is known. ($\text{R} = \text{CH}_3$, R_3P is a monodentate ligand)

(i) What does this indicate about the stereochemistry around the nickel atom?

..... [1]

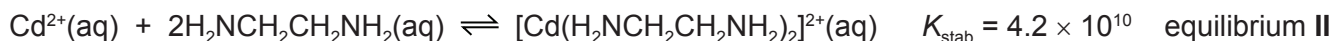
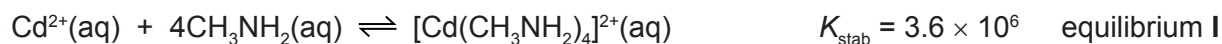
(ii) Draw a three-dimensional diagram showing the structure of this complex.



[1]

[Total: 6]

5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.



(a) (i) Write an expression for the stability constant, K_{stab} , for equilibrium I, and state its units.

$$K_{\text{stab}} =$$

units [2]

Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.

(ii) In a sample of ground water the concentration of $\text{Cd}^{2+}(\text{aq})$ is $1.00 \times 10^{-4} \text{ mol dm}^{-3}$.

Calculate the concentration of $\text{CH}_3\text{NH}_2(\text{aq})$ needed to reduce the concentration of $\text{Cd}^{2+}(\text{aq})$ in this dilute solution by a factor of one thousand.

concentration of $\text{CH}_3\text{NH}_2(\text{aq}) = \dots\dots\dots \text{mol dm}^{-3}$ [2]

- (b) Values for ΔH° and ΔG° for equilibria I and II, and the value of ΔS° for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

- (i) Suggest a reason why the ΔH° values for the two equilibria are very similar.

.....
 [1]

- (ii) Calculate ΔS° for equilibrium II.

$$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [1]$$

- (iii) Suggest a reason for the difference between the ΔS° you have calculated for equilibrium II and that for equilibrium I given in the table.

.....

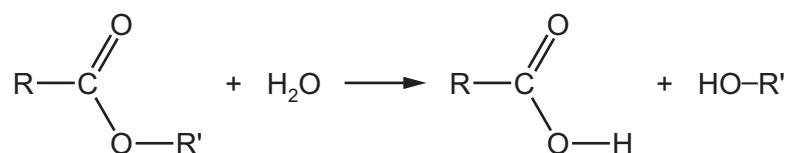
 [1]

- (iv) Which of the two complexes is the more stable? Give a reason for your answer.

.....
 [1]

[Total: 8]

- 6 Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$, but not its isomer methyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$.

- (a) Outline how enzymes catalyse reactions, and explain their specificity.
Use diagrams in your answer where appropriate.

.....

.....

..... [3]

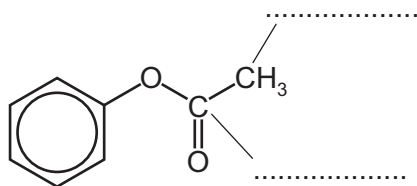
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer **A** and isomer **B**.

(i) The carbon-13 NMR spectra of isomers **A** and **B** contain the following peaks.

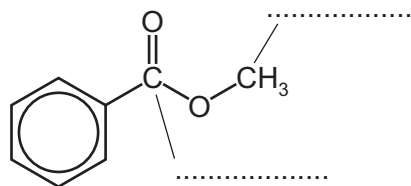
isomer A	isomer B
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



phenyl ethanoate is isomer



methyl benzoate is isomer

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.

You should state the reagents and conditions for each step, and any observations you would make.

step 1

.....

.....

step 2

.....

.....

[3]

[Total: 8]

7 (a) Amino acids can be separated by electrophoresis.

(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.

[3]

(ii) Explain the principles of the separation of amino acids by electrophoresis.

.....

 [2]

(b) Electrophoresis is usually carried out in a buffer solution.

Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures.

Your reasons should refer to the structure of each molecule.

(The structures of these amino acids are given in the *Data Booklet*.)

(i) Asp and Val

buffer pH
 reason

(ii) Lys and Ser

buffer pH
 reason

(iii) Tyr and Phe

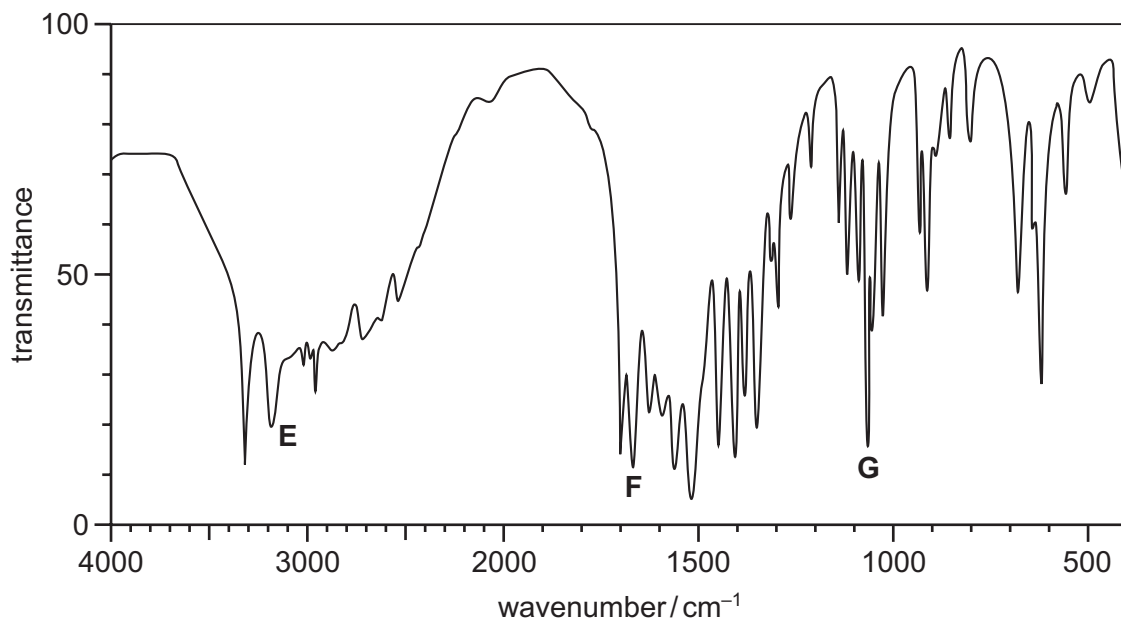
buffer pH
 reason

[3]

(c) (i) Draw the structure of the dipeptide Gly-Ser, showing the peptide bond in full.

[2]

The infra-red spectrum of Gly-Ser is shown below.



(ii) Use the *Data Booklet* to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.

E

F

G

[2]

[Total: 12]

- 8 (a) Describe and explain the trend in the solubility of the hydroxides down Group 2.

.....

.....

.....

..... [3]

- (b) Calcium reacts vigorously with $\text{HCl}(\text{aq})$ producing $\text{H}_2(\text{g})$.

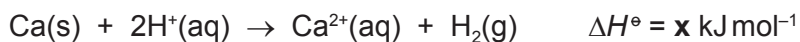


- (i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where $\text{HNO}_3(\text{aq})$ is used in place of HCl but all other conditions are the same?
Explain your answer.

.....

..... [1]

(ii) The ionic equation for this reaction is shown.



Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, **and** data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H_{\text{at}}^\ominus(\text{Ca})$	+178 kJ mol ⁻¹
standard enthalpy of hydration of Ca ²⁺ (g), $\Delta H_{\text{hyd}}^\ominus(\text{Ca}^{2+})$	-1576 kJ mol ⁻¹
standard enthalpy of hydration of H ⁺ (g), $\Delta H_{\text{hyd}}^\ominus(\text{H}^+)$	-1090 kJ mol ⁻¹

x = ... kJ mol⁻¹ [4]

(c) The standard enthalpy change for the reaction between Ca(s) and CH₃CO₂H(aq) is **less negative** than **x** by 2 kJ mol⁻¹.

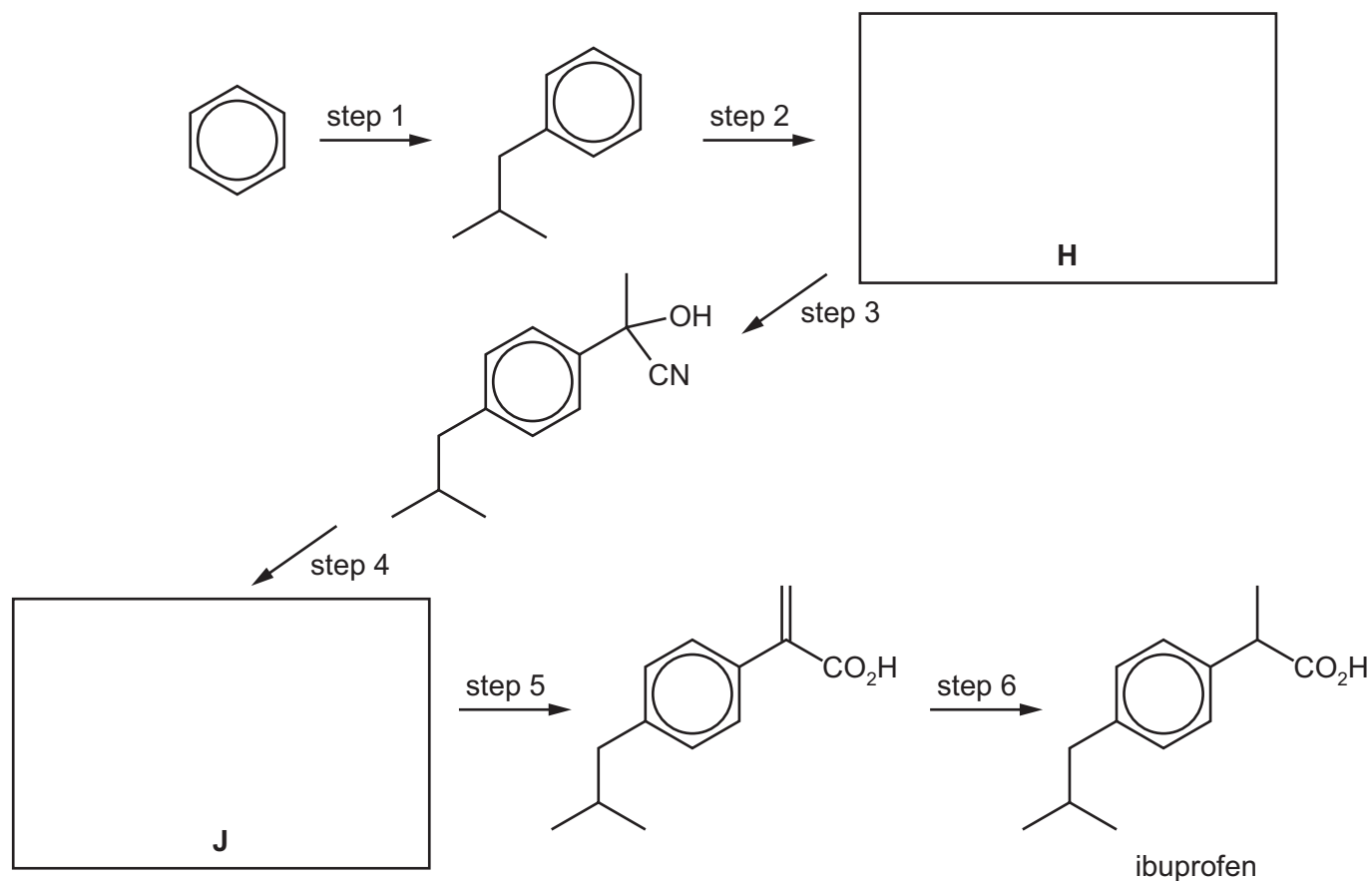
Suggest an explanation for this.

.....

..... [2]

[Total: 10]

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds **H** and **J** and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1

step 2

step 3

step 4

step 5

step 6

[6]

(d) Name the mechanism of step 1 and state the *type of reaction* for step 6.

step 1

step 6

[2]

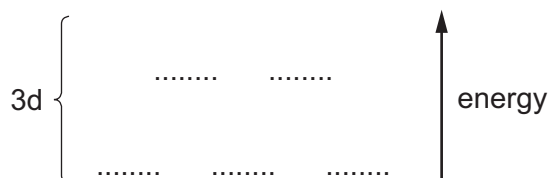
[Total: 11]

10 (a) (i) Complete the electronic configuration of the iron atom.

Fe $1s^2 2s^2 2p^6$ [1]

(ii) In some of its complexes, the Fe^{3+} ion has **only one** unpaired electron in its d orbitals.

Using the symbols $\uparrow$ and $\downarrow$ to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of **this** Fe^{3+} ion.



[1]

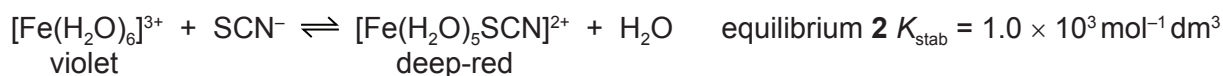
(b) A solution containing a mixture of $\text{Sn}^{2+}(\text{aq})$ and $\text{Sn}^{4+}(\text{aq})$ is added to a solution containing a mixture of $\text{Fe}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$.

Use E° data from the *Data Booklet* to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.

.....

 [2]

- (c) Hexaaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^- , equilibrium **1**, and a deep-red complex with thiocyanate ions, SCN^- , equilibrium **2**.



- (i) Predict and explain the **sequence** of colour changes you would observe in each of the following experiments.

- A few drops of $KSCN(aq)$ are added to 5 cm^3 of $Fe^{3+}(aq)$, followed by a few drops of $KF(aq)$.

.....

- A few drops of $KF(aq)$ are added to 5 cm^3 of $Fe^{3+}(aq)$, followed by a few drops of $KSCN(aq)$.

.....

[4]

- (ii) What *type of reaction* is occurring during the experiments in (i)?

..... [1]

[Total: 9]

Permission to reproduce items where third-party owned material protected by copyright is included has been sought and cleared where possible. Every reasonable effort has been made by the publisher (UCLES) to trace copyright holders, but if any items requiring clearance have unwittingly been included, the publisher will be pleased to make amends at the earliest possible opportunity.

To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced online in the Cambridge International Examinations Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download at www.cie.org.uk after the live examination series.

Cambridge International Examinations is part of the Cambridge Assessment Group. Cambridge Assessment is the brand name of University of Cambridge Local Examinations Syndicate (UCLES), which is itself a department of the University of Cambridge.

CANDIDATE
NAME

--

CENTRE
NUMBER

--	--	--	--	--

CANDIDATE
NUMBER

--	--	--	--

* 1 5 1 6 7 5 5 0 5 3 *



CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

May/June 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **17** printed pages and **3** blank pages.



Answer **all** the questions in the spaces provided.

- 1 (a) Limewater is a saturated solution of $\text{Ca}(\text{OH})_2$ in water. It is used to test for the presence of CO_2 in a gaseous mixture.

(i) Write an equation for the reaction between limewater and CO_2 .

..... [1]

A saturated solution of $\text{Ba}(\text{OH})_2$ can be used instead of $\text{Ca}(\text{OH})_2$ to test for CO_2 . A saturated solution of $\text{Mg}(\text{OH})_2$ cannot be used for this test.

(ii) Explain why a saturated solution of $\text{Ba}(\text{OH})_2$ **can** be used to test for CO_2 .

.....
 [1]

(iii) Explain why a saturated solution of $\text{Mg}(\text{OH})_2$ **cannot** be used to test for CO_2 .

.....

 [2]

(b) Describe and explain the trend in the thermal stabilities of the carbonates down Group 2.

.....

 [3]

(c) Nickel carbonate, NiCO_3 , decomposes on heating.

Use the *Data Booklet* to explain whether NiCO_3 will decompose more or less readily than CaCO_3 .

.....

 [2]

[Total: 9]

2 (a) (i) Complete the following electronic configurations.

- the cobalt atom, Co $1s^2 2s^2 2p^6$
- the cobalt(II) ion, Co^{2+} $1s^2 2s^2 2p^6$

[1]

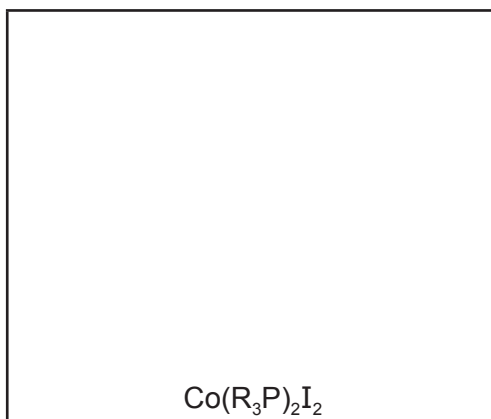
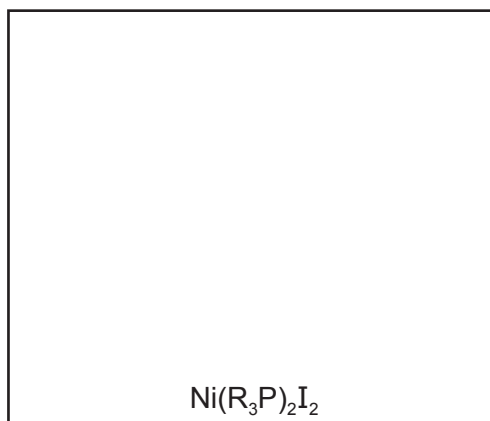
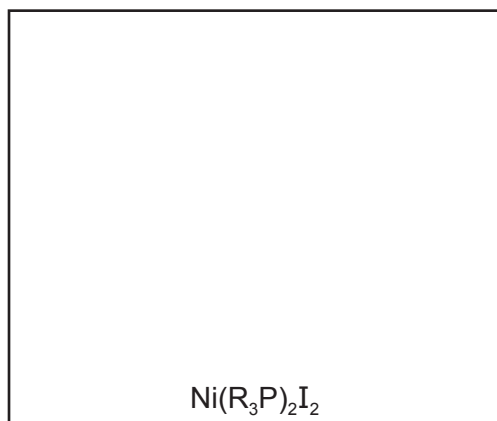
(ii) State the colours you would observe when concentrated $HCl(aq)$ is added to an aqueous solution of cobalt(II) nitrate, $Co(NO_3)_2$.
Give the formulae and geometry of the complexes formed.

.....

 [5]

(b) There are two isomers with the formula $Ni(R_3P)_2I_2$, but only one structure with the formula $Co(R_3P)_2I_2$. (R = alkyl, R_3P is a monodentate ligand)

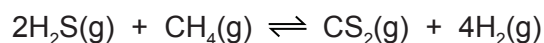
Draw diagrams showing the structure of $Co(R_3P)_2I_2$ and the two isomers of $Ni(R_3P)_2I_2$.



[3]

[Total: 9]

- 3 One method of producing hydrogen from natural gas is the reaction between hydrogen sulfide and methane.



- (a) Write the expression for K_p for this reaction, and state its units.

$$K_p =$$

units
[2]

- (b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.



The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $\text{CS}_2(\text{g})$ is 2 atm and that of the remaining $\text{CH}_4(\text{g})$ is 98 atm.

- (i) Calculate the equilibrium partial pressures of $\text{H}_2\text{S}(\text{g})$ and $\text{H}_2(\text{g})$.

$$p(\text{H}_2\text{S}) = \dots\dots\dots \text{ atm}$$

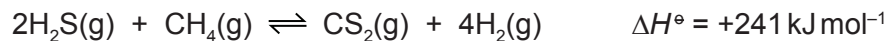
$$p(\text{H}_2) = \dots\dots\dots \text{ atm}$$

[2]

- (ii) Calculate the value of K_p at this temperature.

$$K_p = \dots\dots\dots [1]$$

(c) (i) Predict the sign of ΔS° for this reaction. Explain your answer.



.....
 [1]

The free energy change, ΔG° , for this reaction at 1000 K is $+51 \text{ kJ mol}^{-1}$.

(ii) Calculate the value of ΔS° for this reaction, stating its units.

$\Delta S^\circ =$ units [2]

(d) How would the value of ΔG° , and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

.....

 [2]

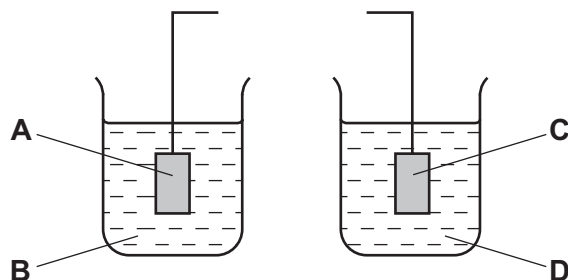
[Total: 10]

- 4 (a) (i) Define the term *standard cell potential*, $E_{\text{cell}}^{\ominus}$.

.....

 [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E_{\text{cell}}^{\ominus}$ for a cell composed of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Ag^{+}/Ag half-cells.



- (ii) Complete the diagram, labelling the components you add. [1]

- (iii) Identify the components A-D.

A
 B
 C
 D [3]

- (b) (i) Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in (a) are connected by a wire and the circuit is completed.

.....
 [1]

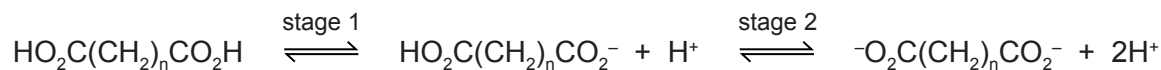
- (ii) Another electrochemical cell was set up using $0.31 \text{ mol dm}^{-3} \text{ Ag}^{+}(\text{aq})$ instead of the standard Ag solution.

Use the Nernst equation, $E = E^{\ominus} + 0.059 \log[\text{Ag}^{+}(\text{aq})]$, and the relevant $E^{\ominus}$ values to calculate the new E_{cell} in this experiment.

$$E_{\text{cell}} = \dots\dots\dots \text{ V [2]}$$

[Total: 8]

5 Dicarboxylic acids dissociate in stages.



(a) The $\text{p}K_{\text{a}}$ values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$	$\text{p}K_{\text{a}}(1)$ for stage 1	$\text{p}K_{\text{a}}(2)$ for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the $\text{p}K_{\text{a}}$ of ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, is 4.76.

(i) State the mathematical relationship between $\text{p}K_{\text{a}}$ and the acid dissociation constant K_{a} .
 [1]

(ii) With reference to the table above, suggest why the $\text{p}K_{\text{a}}(1)$ values

- are all smaller than the $\text{p}K_{\text{a}}$ of ethanoic acid,

.....

- become larger as n increases.

..... [3]

(iii) Suggest why all the $\text{p}K_{\text{a}}(2)$ values in the table above are larger than the $\text{p}K_{\text{a}}$ of ethanoic acid.

.....
 [1]

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

(i) Explain what is meant by the term *buffer solution*.

.....
 [2]

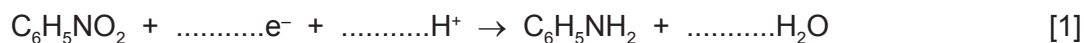
(ii) Write two equations to show how monosodium butanedioate, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na}$, acts as a buffer.

.....
 [2]

[Total: 9]

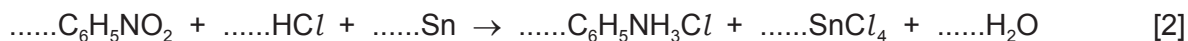
- 6 Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be reduced to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, in acid solution in a two step process.

- (a) (i) Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.



- (ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to (i) useful.



- (b) When 5.0g of nitrobenzene was reduced in this reaction, 4.2g of phenylammonium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = $\dots\dots\dots\%$ [2]

- (c) Following the reaction in (b), an excess of NaOH(aq) was added to liberate phenylamine from phenylammonium chloride.

- (i) Calculate the mass of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, produced when 4.20g of phenylammonium chloride reacts with an excess of NaOH(aq) .

mass of phenylamine = $\dots\dots\dots\text{g}$ [1]

The final volume of the alkaline solution of phenylamine in (i) was 25.0 cm^3 . The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68g of phenylamine.

- (ii) Use the data to calculate the partition coefficient, $K_{\text{partition}}$, of phenylamine between dichloromethane and water.

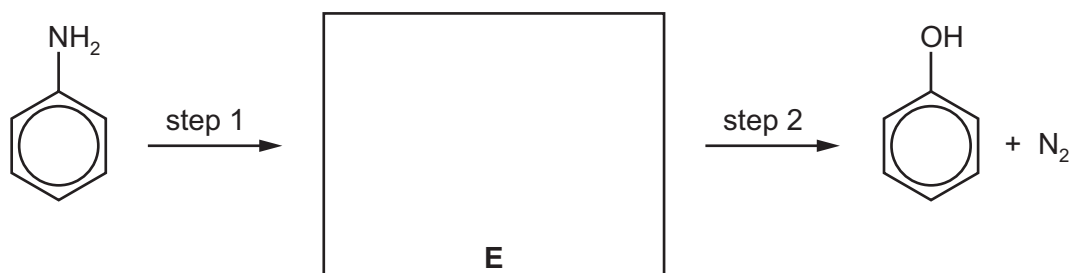
$K_{\text{partition}} = \dots\dots\dots$ [2]

(d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

.....

 [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1
 step 2 [2]

(ii) Draw the structure of the intermediate compound **E** in the box above. [1]

[Total: 13]

- 7 (a) (i) Use the *Data Booklet* to draw the structure of the tripeptide Ala-Ser-Gly showing its peptide bonds in full.

Ala-Ser-Gly

[2]

- (ii) Calculate the relative molecular mass, M_r , of Ala-Ser-Gly.

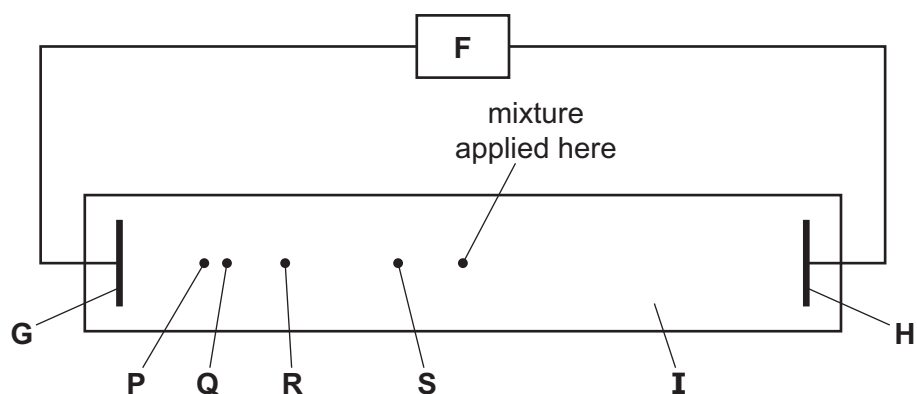
$M_r = \dots\dots\dots$ [1]

- (b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

- (i) Draw the structure of serine at pH 11.

[1]

At the end of the experiment the following results were seen.



(ii) Identify the components labelled **F-I** in the above diagram.

F

G

H

I

[4]

(iii) Suggest the identities of the species responsible for

spot **P**, ...

spot **S**.

Explain your answers.

.....

..... [3]

(c) (i) State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

..... [1]

(ii) Name the *type of reaction* in (i).

..... [1]

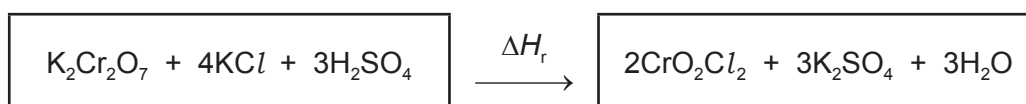
[Total: 13]

- 8 (a) Chromyl chloride, CrO_2Cl_2 , can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.



Use the following data to complete the Hess' Law cycle and calculate the enthalpy change of the reaction, ΔH_r .

compound	enthalpy change of formation, $\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{K}_2\text{Cr}_2\text{O}_7$	−2061
KCl	−437
H_2SO_4	−814
CrO_2Cl_2	−580
K_2SO_4	−1438
H_2O	−286



elements

$\Delta H_r = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

(b) There are two isomeric complex ions with the formula $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$. One is green and the other is violet.

(i) Suggest the *type of isomerism* shown by these complex ions.

..... [1]

(ii) Explain why these two complex ions

- are coloured, ...

.....

.....

.....

- have **different** colours.

.....

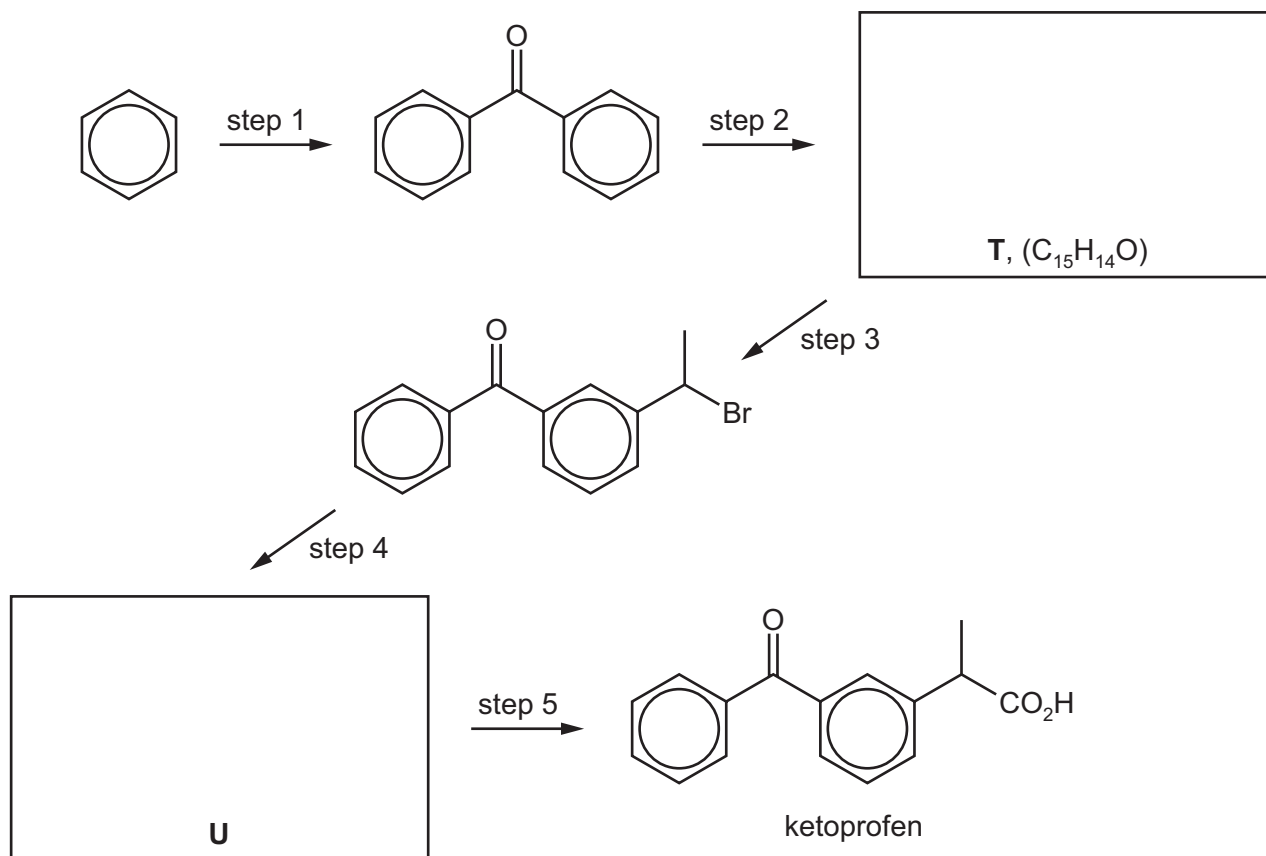
.....

.....

[4]

[Total: 7]

- 9 The anti-inflammatory drug ketoprofen can be synthesised from benzene via the following five steps.



- (a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above.

[2]

- (b) Suggest reagents and conditions for steps 1-5.

step 1

step 2

step 3

step 4

step 5

[5]

- (c) What *types of reaction* are steps 1 and 5?

step 1

step 5

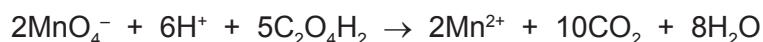
[2]

[Total: 9]

10 (a) Ethanedioic acid, $\text{C}_2\text{O}_4\text{H}_2$, occurs in many vegetables. The amount that occurs in spinach can be estimated as follows.

- 40.0 g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm^3 with water.
- A 25.0 cm^3 portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with $0.0200\text{ mol dm}^{-3}\text{ KMnO}_4$.

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.



In the titration, 15.20 cm^3 of KMnO_4 was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves.

percentage of ethanedioic acid = ... % [3]

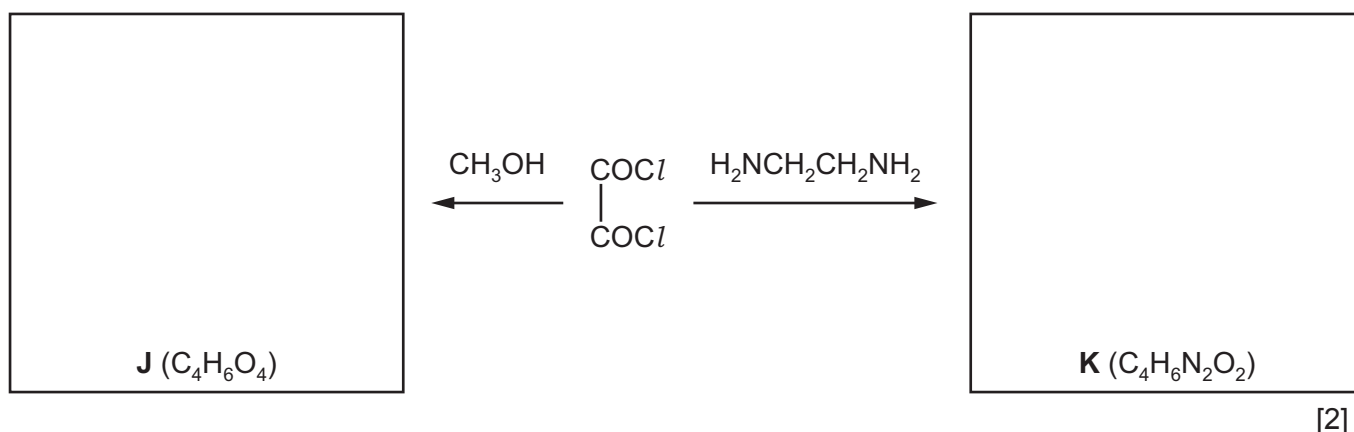
(b) Ethanedioic acid can be converted into ethanedioyl chloride:



(i) State a suitable reagent for this reaction.

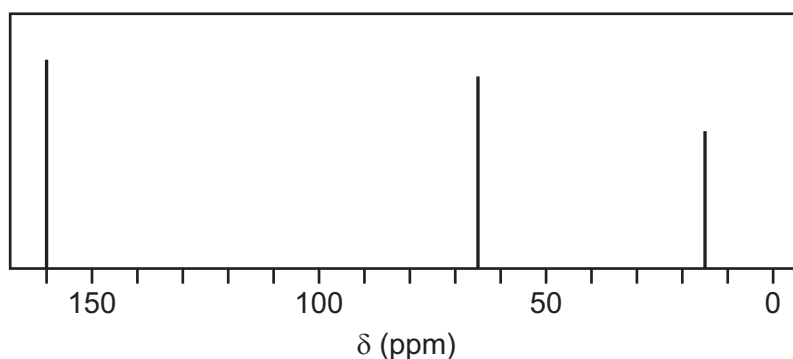
..... [1]

(ii) For the reactions of ethanedioyl chloride below, suggest the structures of compounds **J** and **K** and draw them in the boxes.

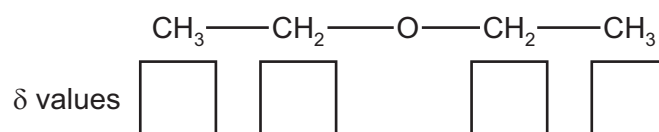


(c) When ethanedioyl chloride is reacted with silver ethanedioate, $\text{AgO}_2\text{CCO}_2\text{Ag}$, in ethoxyethane at -30°C , an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6 .

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, is shown below.



(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.

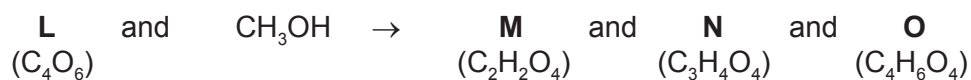


[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.

..... [1]

(d) When pure **L** is reacted with an excess of CH_3OH , a mixture of three compounds is formed.

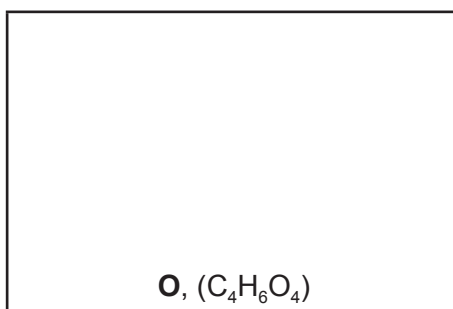
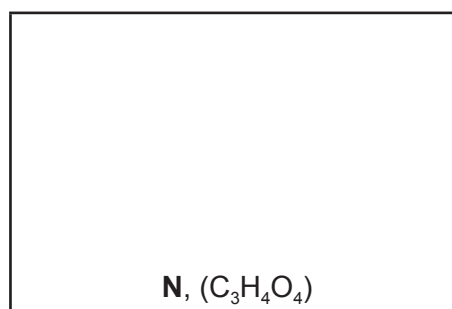
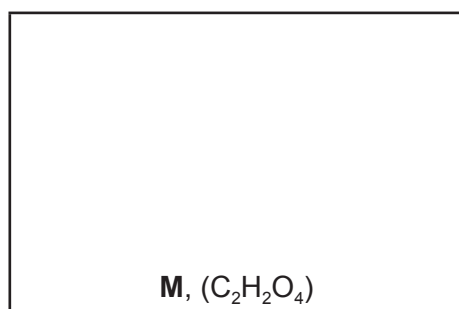


M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

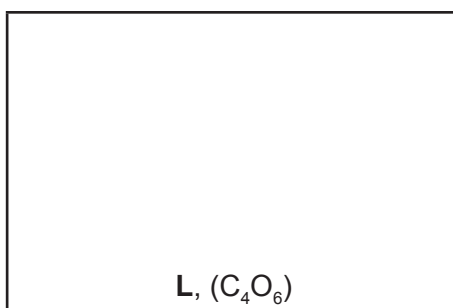
compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Suggest the structures of **M**, **N** and **O**.



[3]

(ii) Suggest a structure for **L** that fits all the data given in (c) and (d).



[1]

[Total: 13]

BLANK PAGE

BLANK PAGE

Permission to reproduce items where third-party owned material protected by copyright is included has been sought and cleared where possible. Every reasonable effort has been made by the publisher (UCLES) to trace copyright holders, but if any items requiring clearance have unwittingly been included, the publisher will be pleased to make amends at the earliest possible opportunity.

To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced online in the Cambridge International Examinations Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download at www.cie.org.uk after the live examination series.

Cambridge International Examinations is part of the Cambridge Assessment Group. Cambridge Assessment is the brand name of University of Cambridge Local Examinations Syndicate (UCLES), which is itself a department of the University of Cambridge.